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(54) Telomers of 1,2-dichloro-1,2-difluoroethylene and process for preparing them.

(57) The present invention relates to telomers of 1,2-dichloro-1,2-difluoroethylene and to a process of preparing them.

1,2-dichloro-1,2-difluoroethylene is reacted, at a temperature of from -100°C to +50°C, with a perhalofluorooxy compound of formula

R_x-OF

wherein

R_x represents, among other, a perhaloalkyl radical of from 1 to 10 carbon atoms.

Telomers are obtained which have, among others, the formulae

R_XO-$(CFCl)_n$-F

R_xO-$(CFCl)_n$-OR_x

R_y-$(CFCl)_n$-F and

F-$(CFCl)_n$-F,

wherein

R_y represents, among others, a perhaloalkyl radical containing from 1 to 9 carbon atoms.

Most of the resulting telomers are new products.

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TELOMERS OF 1,2-DICHLORO-1,2-DIFLUOROETHYLENE AND PROCESS FOR PREPARING THEM

The present invention relates to telomers of 1,2-dichloro-1,2-difluoroethylene.

More particularly, it relates to telomers obtained by reacting 1,2-dichloro-1,2-difluoroethylene with perhalofluorooxy compounds.

One object of the present invention is to provide a process which affords telomers of 1,2-dichloro-1,2-difluoroethylene which contain, besides end groups consisting of fluorine atoms, end groups of both the perhaloalkoxy, i.e., ether type (which, hence, are linked to the monomer units through an oxygen-carbon bond) and of the perhaloalkyl type (i.e., linked to the monomer units through a carbon-carbon bond).

Another object is the provision of a process capable of yielding telomers of 1,2-dichloro-1,2-difluoroethylene which contain a controllable, preferably high proportion of fluorine atoms as end groups.

A further object is to provide telomers in which the nature and the percent distribution of the end groups can be varied within a wide range.

Still a further object is to provide a process by which it is possible, within certain limits, to direct the telomerization reaction towards the formation of telomeric species having a low degree of telomerization or, on the contrary, a relatively high degree of telomerization.

Thus, the present invention is to provide a very flexible process, capable of affording a very wide range of products having different physical and chemical characteristics, which products can be employed in various fields of application.

These and further objects are achieved by the process for preparing telomers of 1,2-dichloro-1,2-difluoroethylene according to the present invention. This process is characterized in that 1,2-dichloro-1,2-difluorethylene is reacted, at a temperature of from about -100 °C to about +50 °C, with a perhalofluorooxy compound of formula

R_x-OF

wherein

R_x represents a linear or branched perhalogenated alkyl, perhaloalkylmonoether or perhaloalkylpolyether radical of from 1 to 10 carbon atoms, which contains fluorine atoms or fluorine and chlorine atoms.

It is assumed that the reaction starts with the homolytic breakage of the O-F bond of the fluorooxy compound according to the scheme:

$R_x\text{-}OF \rightarrow R_x\text{-}O\cdot + F\cdot$

resulting in R_x-O· and F· radicals which can act as initiators and terminators of telomerization.

Probably, the above R_x-O· radicals which contain more than one carbon atom are also capable of undergoing further fragmentation and rearrangement reactions with other radical species being formed which, in turn, can also act as telomerization initiators and terminators.

Hence, by starting from a perhaloflurooxy compound, one can form radicals R^1 derived from radicals R_x, in which R_x of at least two carbon atoms has lost at least one carbon atom and/or R_x of at least 3 carbon atoms has undergone a rearrangement. More commonly, the radical R^1 is a radical R_y containing a lower number of carbon atoms than R_x. Thus, when R_x contains from 2 to 10 carbon atoms, R_y contains from 1 to 9 carbon atoms.

Furthermore, during the chain growth reaction, the teleomeric radicals are presumably capable of undergoing exchange reactions with other radicals with, for example, C1 radicals being formed which, in turn, can act as telpmerization initiators and terminators. The above exchange reactions can be particularly promoted when the reaction is carried out in the presence of F_2, according to the procedure described below.

Rearrangement reactions of the telomeric radicals can also occur with terminal double bonds being formed according to the scheme:

$-CFCl\text{-}CFCl\cdot \rightarrow -CF=CFCl + Cl\cdot$

It has been found according to the present invention that the telomerization products are composed of a mixture of telomers having different end groups and different degrees of telomerization.

When the reaction is carried out in the absence of fluorine, the telomers obtained are predominantly the following:

$R_xO-(CFCl)_n-F$	(A)
$R_xO-(CFCl)_n-OR_x$	(B)
$R_y-(CFCl)_n-F$	(C)
$F-(CFCl)_n-F$	(D)

wherein:
n ranges from 4 to 20;
R_x is defined as specified above;
R_y is a radical derived from R_x, wherein R_x containing at least two carbon atoms has lost at least one carbon atom; therefore, R_y is a linear or branched perhalogenated alkyl radical, a perhaloalkylomonether radical or a perhaloalkylpolyether radical of from 1 to 9 carbon atoms, which contains fluorine atoms or fluorine and chlorine atoms.

The telomers (A), (B) and (C) are new products.

In addition to the above, small amounts of the following telomers, characterized by an unsaturation in chain-end position can also be present.

$R_xO-(CFCl)_{n-2}-CF=CFCl$	(Q)
and	
$F-(CFCl)_{n-2}-CF=CFCl$	(R)

The telomers (Q) are also new products.

When the reaction is carried out in the presence of fluorine and at rather high temperatures under conditions as defined below the following telomers are also formed:

$R_xO-(CFCl)_n-Cl$	(E)
$F-(CFCl)_n-Cl$	(F)
$Cl-(CFCl)_n-Cl$	(G)
$F-[(CFCl)_{n-1}CF_2]-F$	(H)
$F-[(CFCl)_{n-1}CF_2]-OR_x$	(I)
$R_xO-[(CFCl)_{n-m}(CF_2)_m]-OR_x$	(L)
$R_xO-[(CFCl)_{n-m}(CF_2)_m]-Cl$	(M)
$R_y-[(CFCl)_{n-m}(CF_2)_m]-Cl$	(N)
$F-[(CFCl)_{n-m}(CF_2)_m]-Cl$	(O)
$Cl-[(CFCl)_{n-m}(CF_2)_m]-Cl$	(P)

wherein m is 1 or 2.

In the telomers (H), (I), (L), (M), (N), (O) and (P) the CF_2 groups can be in any position along the chain of monomer units.

The telomers (E), (I), (L), (M) and (N) are new products.

In the telomer mixtures obtained, both in the presence and in the absence of fluorine, small amounts of telomers, having formulae different from the ones shown above may also be present.

When R_x and R_y are perhaloalkylpolyether radicals, they preferably contain two oxygen atoms.

The radicals R_x and R_y preferably are perfluorinated radicals.

Preferably, R_x contains from 1 to 6 carbon atoms while R_y contains from 1 to 5 carbon atoms.

When R_x and R_y contain chlorine atoms, they preferably do not contain $-CCl_3$ groups.

In the preferred products n generally ranges from 4 to 10.

In order to carry out the reaction, generally an either gaseous or liquid stream of perhalofluorooxy compound is introduced into a reactor which contains 1,2-dichloro-1,2-difluorethylene either in the liquid state or dissolved in a suitable solvent. Since the boiling point of 1,2-dichloro-1,2-difluoroethylene is about +22 °C, the reaction should suitably be carried out below said temperature. In case pressures higher than atmospheric pressure (under which 1,2-dichloro-1,2-difluoroethylene can be kept in the liquid state) are used, the reaction can be carried out at temperatures higher than + 22 °C.

If the reaction is to be carried out in solution, a solvent for 1,2-dichloro-1,2-difluoroethylene, which is inert under the reaction conditions, can be used. In particular, a chlorofluorocarbon such as, for example,

1,2-dichlorotetrafluoroethane, fluorotrichloromethane and dichlorodifluoromethane may be employed for this purpose. The concentration of 1,2-dichloro-1,2-difluoroethylene in the solution generally ranges from 20 to 95% by weight.

Generally, the fluorooxy compound is fed to the reactor in the form of a gaseous stream. The gaseous fluorooxy compound preferably is diluted with a gas inert under the reaction conditions. Examples of inert diluent gases are nitrogen, argon, helium and gaseous chlorofluorocarbons, selected, for example, from 1,2-dichlorotetrafluoroethane, dichlorodifluoromethane and mixtures thereof. When the fluorooxy compound is CF_3OF, it can be fed in the absence of an inert gas or in the presence of any amount of an inert gas, i.e., CF_3OF can be used at a concentration of from 0.01% to 100% by volume, based on the mixture of CF_3OF and inert gas.

When the reaction is carried out with fluorooxy compounds containing at least two carbon atoms, the concentration of the fluorooxy compound in the mixture of said fluorooxy compound and inert gas generally is from 0.05% to 25% by volume.

When the reaction is carried out in the presence of fluorine, the amount of said fluorine generally ranges from 10 to 90 parts by volume per 100 parts of mixture of fluorine and fluorooxy compound. Smaller amounts of fluorine can also be used (for example, from 1 to 10 parts by volume per 100 parts of mixture of fluorine and fluorooxy compound) but under such conditions the influence of fluorine on the nature of the terminal groups obtained is less pronounced.

If the fluorooxy compound is fed to the reactor in the liquid state, it is mixed with a liquid inert under the reaction conditions, in particular a chlorofluorocarbon, for example 1,2-dichlorotetrafluoroethane, fluorotrichloromethane and dichlorodifluoromethane (or mixtures thereof) and is carried, in aerosol form, by a gas inert under the reaction conditions, for example, nitrogen, argon or helium.

To the reactor containing a solvent for 1,2-dichloro-1,2-difluoroethylene a stream of fluorooxy compound in the gaseous or liquid state can be fed according to any of the feeding procedures outlined above, with a stream of 1,2-dichloro-1,2-difluoroethylene in gaseous or liquid form being introduced simultaneously. In this case, 1,2-dichloro-1,2-difluoroethylene is preferably employed in the liquid state.

Of course, other procedures can be used in order to bring the reactants into contact with each other. For example, liquid 1,2-dichloro-1,2-difluoroethylene can be fed to a reactor containing the fluorooxy compound dissolved in a suitable solvent, in particular dissolved in a chlorofluorocarbon selected from, for example, 1,2-dichlorotetrafluoroethane, fluorotrichloromethane, dichlorodifluoromethane and mixtures thereof.

The temperature at which the reaction is carried out ranges from about -100 °C to about +50 °C. For each fluorooxy compound, the reaction should be carried out at a temperature which is at least equal to the threshold temperature of its reaction with 1,2-dichloro-1,2-difluoroethylene. Said threshold temperature is different for each telogen. Preferably, the reaction is carried out at a temperature within the range of from -100 °C to -20 °C.

The reaction can be directed so that is predominantly yields the telomeric species (A), (B), (C) and (D). This result can be obtained by operating in the absence of elemental fluorine or in the presence of small amounts thereof (for example, within the range of from 1 to 3% by volume in the mixture of fluorooxy compound and F_2) and, simultaneously, under such conditions as to decrease the amount of heat development inside the reaction medium.

These conditions are:

(a) An effective stirring of the reaction medium;

(b) Use of reaction temperatures within a relatively low range, provided that they are still higher than the threshold reaction temperature, i.e., in particular, use of temperatures of from -100 up to -60 °C;

(c) Reduction of the telogen flowrate;

(d) Increasing the telogen dilution.

In order to obtain the above result, condition (a) is coupled with one or more (all) of conditions (b), (c) and (d).

By operating according to the above procedure, said telomers (A), (B), (C) and (D) can be obtained in proportions which may reach, or even exceed, 90% by weight of the total of reaction products.

The reaction can also be directed towards the formation of relatively large amounts of telomers (C), i.e., of those containing an end group of the perhaloalkyl type, by operating with less intense stirring and at higher temperatures of the reaction medium (in particular within the range of from -40 to -60 °C).

The same result can be obtained by using a higher flowrate of the telogen, at lower temperatures (for example, of from -60 to -80 °C) and with a lower degree of dilution of the telogen in the inert gas.

By operating in the presence of large amounts of elemental fluorine (within the range of from 10 to 50 parts by volume of F_2 per 100 parts of mixture of F_2 and the fluorooxy compound) and at relatively high

temperatures (within the range of from -60° C to about -20° C), the proportion of telomers containing end groups -F and -Cl, in particular of the species (D), (F), (G), (O) and (P), can be increased.

By operating in the presence of large amounts of elemental fluorine (within the range of from 25 to 95 parts by volume of F_2 per 100 parts of mixture of F_2 and fluorooxy compound), at lower temperatures (within the range of from -100° C up to about -60° C) and with high degree of dilution of fluorooxy compound and fluorine in the carrier gas, a high proportion of telomers may be obtained wherein one or both end groups are -F. The expression "high degree of dilution of fluorooxy compound" is meant to indicate, for example, 1 to 3 parts by volume of the total amount of fluorooxy compound and elemental fluorine per 100 parts of diluent gas. By operating according to these modalities, in particular the telomers (A), (B) and (D) with a large proportion of the (D) species can be obtained.

According to a further aspect of the process of the present invention, when adopting the conditions under which the telomerization reaction can be directed towards the prevailing formation of the desired telomeric species, the degree of telomerization can, furthermore, be directed, within certain limits, towards low values. Said result can be achieved by using one or more (or all) of the following conditions:

- Low telogen flowrates;
- Relatively high degree of dilution of the telogens;
- Low reaction temperature;
- Use of 1,2-dichloro-1,2-difluoroethylene in the presence of a solvent thereof.

For example, by adopting the above conditions, more than 95% of the telomers having values of n within the range of from 4 to 6 can be obtained.

The products obtainable by the process according to the present invention can be used as electrical insulators, lubricants and heat transfer media.

They are, furthermore, intermediate products for the preparation, by de-chlorination, of olefinic products, for example, perfluorobutadiene, disclosed in copending European patent application, case No. D3814 (which is being filed on the same day as the instant one) by applicant. These olefinic products are useful for preparing polymeric products, dielectric fluids and heat exchange fluids. In these applications, the end products obtained by means of the process according to the present invention can be used as obtained, i.e., as mixtures or, after an enrichment - by distillation - with certain components, for example, with components having a low degree of telomerization. Furthermore, as already explained, the use of particular operating conditions makes it possible to obtain mixtures which contain relatively large amounts of one or more specific telomeric species.

The presence of a considerable amount of determined end groups (perhaloalkoxy, perhaloalkyl, -Cl, -F) or of a prevailing amount of -F end groups as well as the prevalence of a relatively low or relatively high degree of telomerization and the possibility of varying the telogen employed as starting material afford various ranges of products with particular physico-chemical properties. Said properties make it possible to employ the telomeric products in various fields of application.

Examples of specific fluorooxy compounds which can be used in the process of the present invention include:

fluorooxy trifluoromethane;
fluorooxy pentafluoroethane;
1-fluorooxy heptafluoropropane;
1-fluorooxy nonafluorobutane;
1-fluoro-2-chlorotetrafluoroethane;
1-fluorooxy-2,2'-dichlorotrifluoroethane;
fluorooxy heptafluoroisopropane;
fluorooxy nonafluoroisobutane;
fluorooxy nonafluoro-tert.-butane;
1-fluorooxy-2-perfluoro-n-propoxy-hexafluoropropane;
1-fluorooxy-2-perfluoromethoxy-hexafluoropropane;
1-fluorooxy-2-perfluoroethoxy-hexafluoropropane and
1-fluorooxy-3-chloro-hexafluoropropane.

When CF_3OF is used as telogen in the absence or in the presence of small amounts of F_2 (up to 3% by volume in the mixture of CF_3OF and F_2) and of an inert diluent (up to 33% by volume of CF_3OF in the mixture of CF_3OF and N_2), the mixture of telomers obtained is almost exclusively composed of the following species:

$CF_3O-(CFCl)_n-F$	(Ia)
$CF_3O-(CFCl)_n-OCF_3$	(IIa)
$F(CFCl)_n-F$	(IIIa)

(Ia) and (IIa) are new products.

(Ia) and (IIa) may represent more than 90% of the reaction products. Products with values of n of from 4 to 6 can constitute more than 99% of the crude reaction product.

By employing CF_3OF or CF_3OF and F_2 (according to volume ratios of from 1:1 to 1:3) with high degrees of dilution in an inert gas (for example, with a concentration of CF_3OF of about 1%), the species (IIIa) may represent up to 90% of the above species.

When CF_3OF is used as telogen in the presence of large amounts of F_2 (for example, 70% by volume in the mixture of CF_3OF nd F_2) and with low degrees of dilution in an inert diluent gas, at relatively high temperatures (for example about -40 °C), besides the above telomers, the following species are also formed:

$F-(CFCl)_n-Cl$	(IVa)
$Cl-(CFCl)_n-Cl$	(Va)
$CF_3O-(CFCl)_n-Cl$	(VIa)
$F-[(CFCl)_{n-1}CF_2]-F$	(VIIa)
$F-[(CFCl)_{n-1}CF_2]-OCF_3$	(VIIIa)
$CF_3O-[(CFCl)_{n-1}CF_2]-OCF_3$	(IXa)
$F-[(CFCL)_nCF_2]-Cl$	(Xa)
$CF_3O-[(CFCL)_nCF_2]-Cl$	(XIa)
$Cl-[(CFCL)_nCF_2]-Cl$	(XIIa)

(VIa), (VIIIa), (IXa) and (XIa) are new species.

Under the conditions just mentioned the species having initial F and Cl atoms and terminal F and Cl atoms are predominant and can constitute up to and even more than 90% of the telomer mixture obtained. Under these conditions species with values of n equal to 4 can represent up to or even more than 75% of the mixture.

By employing CF_3OF as the telogen and using or not using large amounts of fluorine, small amounts of other species may be formed, such, as, for example:

$F-(CFCl)_{n-2}-CF=CFCl$	(IIIb)
$CF_3O-(CFCl)_{n-2}-CF=CFCl$	(Ib)
$CF_3O-[(CFCl)_{n-1}-CFH]-F$	(I′b)

(Ib) and (I′b) are new species. Species (IIIb) and (Ib) can be formed through the loss of a Cl· radical from the radical chain. Species (I′b) can be formed by substitution of an H atom for a Cl atom in case hydrogen-containing substances (for example, small amounts of water) are present in the reaction medium.

In the species (I′b), the -CFH- group can be in any position along the chain of monomer units.

When CF_3CF_2OF is used as the telogen in the absence, or in the presence of small amounts, of F_2 (up to 17% by volume in the mixture of CF_3CF_2OF and F_2), the mixture of telomers obtained is prevailingly composed of the following species:

$CF_3CF_2O-(CFCl)_n-F$	(Ic)
$CF_3CF_2O-(CFCl)_n-OCF_2CF_3$	(IIc)
$CF_3-(CFCl)_n-F$	(IIIc)
$F-(CFCl)_n-F$	(IIIa)
$CF_3-(CFCl)_n-OCF_2CF_3$	(IVc)
$CF_3CF_2O-(CFCl)_{n-2}-CF=CFCl$	(I′c)

Telomers (Ic), (IIc), (IIIc), (IVc) and (I′c) are new products.

When CF_3-CF_2-CF_2-OF is used as the telogen at low temperatures (within the range of from -90 °C up to -75 °C) and in the absence, or in the presence of small amounts, of F_2 (up to 10% by volume in the mixture of CF_3-CF_2-CF_2-OF and F_2), the mixture of telomers obtained is prevailingly composed of the following species (more than 95% of the species present):

$CF_3CF_2CF_2O$-$(CFCl)_n$-F	(Id)
$CF_3CF_2CF_2O$-$(CFCl)_n$-$OCF_2CF_2CF_3$	(IId)
CF_3CF_2-$(CFCl)_n$-$OCF_2CF_2CF_3$	(IIId)
F-$(CFCl)_n$-F	(IIIa)

When CF_3-CF_2-CF_2-OF is used as the telogen, at higher temperatures (within the range of from -40 °C to -65 °C), in the absence, or in the presence of small amounts, of F_2, employing high concentrations (for example, 50%) of 1,2-dichloro-2,3-difluoroethylene in a solvent, the mixture obtained is predominantly composed of the following species:

$CF_3CF_2CF_2O$-$(CFCl)_n$-F	(Id)
$CF_3CF_2CF_2O$-$(CFCl)_n$-$OCF_2CF_2CF_3$	(IId)
CF_3CF_2-$(CFCl)_n$-$OCF_2CF_2CF_3$	(IIId)
F-$(CFCl)_n$-F	(IIIa)
CF_3O-$(CFCl)_n$-F	(Ia)
CF_3O-$(CFCl)_n$-$OCF_2CF_2CF_3$	(IVd)
$CF_3CF_2CF_2O$-$[(CFCl)_{n-m}(CF_2)_m]$-F	(Vd)
$CF_3CF_2CF_2O$-$CF_2CF_2CF_2O$-$(CFCl)_n$-F	(VId)
$CF_3CF_2CF_2O$-$(CFCl)_n$-Cl	(VIId)
F-$[(CFCl)_{n-m}(CF_2)_m]$-F	(VIIId)
CF_3O-$[(CFCl)_{n-m}(CF_2)_m]$-F	(IXd)
CF_3O-$(CFCl)_n$-OCF_3	(IIa)
$CF_3CF_2CF_2O$-$[(CFCl)_{n-m}(CF_2)_m]$-Cl	(Xd)
$CF_3CF_2CF_2O$-$[(CFCl)_{n-1}(CFH)]$-F	(XId)
F-$(CFCl)_{n-2}$-CF = CFCl	(IIIb)
CF_3O-$(CFCl)_{n-2}$-CF = CFCl	(Ib)
$CF_3CF_2CF_2O$-$(CFCl)_{n-2}$-CF = CFCl	(Ie)

wherein m is 1 or 2.

(Id), (IId), (IIId), (Ia), (IVd), (Vd), (VId), (VIId), (IXd), (IIa), (Xd), (XId), (Ib) and (Ie) are new species.

(Id), (IId), (IIIa), (Ia) and (IVd) may represent up to or even more than 70% of the species present.

The main advantages of the process according to the present invention can be summarized as follows:

1. The percent distribution and the nature of the end groups present in the telomeric species obtained can be varied within a wide range and, within certain limits, the degree of telomerization can also be varied. Thus, a very wide range of products having different physical and chemical properties can be obtained which properties are suitable for meeting a host of requirements in many fields of application.

2. When the reaction is carried out in a way such as to result in no or at least very few -Cl end groups, the resulting telomers are endowed with high chemical and thermal stabilities.

The following examples are given in order to illustrate the invention without, however, limiting it.

EXAMPLE 1

A stream of 1.0 Nl/hour of CF_3OF and 2.0 Nl/hour of N_2 was continuously bubbled through 178 g of liquid 1,2-dichloro-1,2-difluoroethylene (DCDFE), cooled at -40 °C, in a reactor equipped with condenser, thermometer and stirrer.

After six hours the reaction was stopped, unreacted DCDPE was distilled off and 45.1 g of product were recovered.

The product was analyzed by gas-chromatography on a 3% SP-2100 column and by gas-mass and ^{18}F-N.M.R. spectroscopy.

The product was composed of the telomeric species (Ia) to (IXa). The species (Ia) and (IIa) represented

more than 90% of the mixture. Species (IIIa) accounted for about 4% of the mixture.

From the gas-chromatographic analysis it was concluded that species having values of within the range of from 4 to 6 constituted about 96% of the crude reaction mixture.

EXAMPLE 2

Following the procedure of example 1, 1.5 Nl/hour of CF_3OF and 3 NL/hour of N_2 were bubbled (for 9 hours) through 178.3 g of DCDFE mixed with 43.7 g of 1,2-dichlorotetrafluoroethane, kept at a temperature of -75° C.

After removal of unreacted DCDFE and solvent, 24.4 g of product were obtained.

The product obtained contained (Ia), (IIa) and (IIIa) as well as traces of $CF_3O\text{-}(CFCl)_2\text{-}CF=CFCl$.

Species (Ia) and (IIa) represented more than 95% of the mixture while the species (IIIa) accounted for about 2% of the reaction product.

Species with n values within the range of from 4 to 6 constituted more than 99% of the crude reaction product.

EXAMPLE 3

Following the procedure of example 1, 1.5 Nl/hour of CF_3OF and 3 Nl/hour of N_2 were bubbled (for 6.5 hours) through 170 g of DCDFE kept at -5° C.

After removing the unreacted DCDFE, 20.5 g of product were obtained.

The product obtained contained the species (Ia), (IIa) and (IIIa)

$CF_3O\text{-}(CFCl)_{n-2}\text{-}CF=CFCl$	(Ib)
and	
$F\text{-}(CFCl)_{n-2}\text{-}CF=CFCl$	(IIIb)

Species (Ia) and (IIa) constituted more than 85% of the mixture, while species (IIIa) constituted about 12% thereof.

Species with n values comprised within the range of from 3 to 6 represented more than 99% of the crude product.

EXAMPLE 4

Following the procedure of example 1, 0.3 Nl/hour of CF_3OF, 0.7 Nl/hour of fluorine and 2 Nl/hour of N_2 were bubbled (for 6 hours) through 151 g of DCDFE kept at -40° C.

After removing the unreacted DCDFE, 12 g of a reaction product composed of species (Ia) to (XIIa) were recovered.

Species (IIIa), (IVa), (Va), (VIIa), (Xa) and (XIIa) constituted more than 00% of the mixture. Species (IIIa) accounted for about 27% of said mixture.

Species with n values of 4 represented about 75% of the crude product.

EXAMPLE 5

Following the procedure of example 1, 1 Nl/hour of CF_3CF_2OF and 5 Nl/hour of N_2 were bubbled through 190 g of 1,2-dichlorotetrafluoroethane containing 10 g of DCDFE, kept at -75° C.

During the whole reaction time of 5 hours additional 28 g of DCDFE were successively added.

After removing the solvent and the unreacted olefin, species (Ic) to (IVc), (I′c) and (IIIa) were present in the crude product.

Among these, (IIIa) accounted for about 20% and (Ic) and (IIc) represented about 70% of the product.

Species with n values within the range of from 4 to 6 constituted about 93% of the product.

EXAMPLE 6

Following the procedure of example 1, 0.8 Nl/hour of $CF_3CF_2CF_2OF$, 0.2 Nl/hour of F_2 and 2.4 Nl/hour of N_2, pre-cooled at -40° C, were bubbled through 45 g of DCDFE, dissolved in 300 g of 1,2-dichlorotetrafluoroethane kept at -75° C.

During the bubbling, additional 63 g of DCDFE were successively added. The total reaction time was 17.5 hours.

After removing the solvent and the unreacted DCDFE, the telomeric product was recovered. Said product was composed of species (Id), (IId), (IIId) and (IIIa).

Species (Id), (IId) and (IIId) represented more than 70% of the mixture while species (IIIa) accounted for about 27%.

Species with n values of 4 constituted about 90% of the crude product.

EXAMPLE 7

Following the procedure of example 6, 1.2 Nl/hour of $CF_3CF_2CF_2OF$, 0.1 Nl/hour of F2 and 5 Nl/hour of N_2 were cooled to -45° C and bubbled through 30 g of DCDFE dissolved in 500 g of CF_2Cl_2, kept at -92° C.

During the reaction 43.5 g of DCDFE were successively added. The total reaction time was 6.5 hours.

After removing the solvent and the unreacted olefin, telomers (Ia), (IIa) and (IIIa), of which the species (IIIa) accounted for 45%, were present.

The species with n values of 4 constituted about 95% of the product.

EXAMPLE 8

Following the procedure of example 6, 1 Nl/hour of $CF_3CF_2CF_2OF$ and 4 Nl/hour of N_2, cooled to -25° C, were bubbled through 110 g of 1,2-dichlorotetrafluoroethane containing 90 g of DCDFE and kept at -65° C.

The total reaction time was 7 hours.

After removal of the solvent and the unreacted olefin, the species (Id), (IId), (IIId), (IIIa), (Ia), (IVd), (Vd), (VId), (VIId), (VIIId), (IXd), (IIa), (Xd), (XId), (IIIb), (Ib) and (Ie) were present in the crude reaction product. Species (IIIa) accounted for about 24% of the product.

Species with n values of 4 constituted about 70% of the product.

EXAMPLE 9

In a reactor equipped with condenser, thermometer and stirrer, a gas stream consisting of 0.6 Nl/hour of F_2 and 103 Nl/hour of N_2 was continuously bubbled through 151 g of liquid DCDFE kept at -72° C.

After 6 hours the reaction was stopped and unreacted DCDFE was distilled off, leaving 37.33 g of product.

Said product was analysed by gas-chromatography on a 3% SP 2100 packed column, by gas mass and, finally by ^{19}F-N.M.R. spectroscopy.

The product was composed of telomers (Ia) to (IIIa).

The species (Ia) and (IIa) represented 13% and the species (IIIa) constituted about 87% of the mixture.

From the gas-chromatographic analysis it was concluded that species with values of n within the range of from 4 to 6 constituted 100% of the crude product.

EXAMPLE 10

In a reactor equipped with condenser, thermometer and stirrer, a gas stream consisting of 1.2 Nl/hour of fluorooxy trifluoromethane and 103 Nl/hour of N_2 was continuously bubbled through 150 g of liquid DCDFE kept at -72° C.

After 6 hours the reaction was stopped and unreacted DCDFE was distilled off, leaving 45 g of product.

Said product was analysed by gas-chromatography on a 3% SP 2100 packed column, by gas mass and, finally by ^{19}F-N.M.R. spectroscopy.

The product was composed of telomers (Ia) to (IXa).

The species (Ia) and (IIa) accounted for about 38% of the mixture while species (IIIa) represented about 58% of the mixture.

From the gas-chromatographic analysis it was concluded that species with values of n within the range of from 4 to 6 represented about 97% of the crude product.

EXAMPLE 11

In a reactor equipped with condenser, thermometer and stirrer a gas stream consisting of 1.2 Nl/hour of fluorooxytrifluoromethane and 103 Nl/hour of N_2 was continuously bubbled through 150 g of a liquid mixture consisting of 75% by weight of DCDFE and 25% of trichlorotrifluoroethane kept at -72° C.

After 6 hours the reaction was stopped and unreacted DCDFE was distilled off, leaving 28.15 g of a mixture of telomers.

The product was analysed by gas-chromatography on a 3% SP 2100 packed column, by gas mass and, finally, by ^{19}F-N.M.R. spectroscopy.

The product was composed of telomers (Ia), (IIa) and (IIIa).

Telomers (Ia) and (IIa) constituted about 17% of the mixture. Species (IIIa) accounted for about 83% of the mixture.

From the gas-chromatographic analysis it was concluded that species with n values of 4 constituted about 98% of the crude product.

Claims

1. Process for preparing telomers of 1,2-dichloro-1,2-difluoroethylene, characterized in that 1,2-dichloro-1,2-difluoroethylene is reacted, at a temperature of from about -100° C to about +50° C, with a perhalofluorooxy compound of formula

R_x-OF

wherein

R_x represents a linear or branched perhaloalkyl, perhaloalkylmonoether or perhaloalkylpolyether radical of from 1 to 10 carbon atoms, which contains fluorine atoms or fluorine and chlorine atoms.

2. Process according to claim 1, characterized in that, when R_x is a perhaloalkylpolyether radical, it contains two oxygen atoms.

3. Process according to claim 1 or 2, characterized in that R_x is a perfluorinated radical or that, when R_x contains chlorine atoms, it does not comprise -CCl_3 groups.

4. Process according to one or more of the preceding claims, characterized in that R_x contains from 1 to 6 carbon atoms.

5. Process according to one or more of the preceding claims, characterized in that a gaseous stream of a perhalofluorooxy compound is introduced into a reactor which contains 1,2-dichloro-1,2-difluoroethylene, either in the liquid state or dissolved in a solvent inert under the reaction conditions, preferably in a chlorofluorocarbon.

6. Process according to one or more of the preceding claims, characterized in that, before being introduced, the perhalofluorooxy compound is diluted with a gas inert under the reaction conditions, preferably nitrogen, argon, helium or a chlorofluorocarbon gas.

7. Process according to one or more of claims 1 to 4, characterized in that the perhalofluorooxy compound is introduced in the liquid state into a reactor which contains 1,2-dichloro-1,2-difluoroethylene, either in the liquid state or dissolved in a solvent inert under the reaction conditions, with the perhalofluorooxy compound being mixed with a liquid inert under the reaction conditions, or being carried as an aerosol, by a gas inert under the reaction conditions, preferably nitrogen, argon or helium.

8. Process according to claim 7, characterized in that the liquid inert under the reaction conditions is a chlorofluorocarbon.

9. Process according to one or more of the preceding claims, characterized in that fluorine is fed to the reaction medium in an amount of from 1 to 90 parts by volume, preferably 10 to 90 parts by volume, per 100 parts of mixture of fluorine and perhalofluorooxy compound.

10. Process according to one or more of the preceding claims, characterized in that the reaction is carried out at a temperature of from about -100° C to about -20° C.

11. Telomers of 1,2-dichloro-1,2-difluoroethylene having the formulae:

$R_xO-(CFCl)_n-F$	(A)
$R_xO-(CFCl)_n-OR_x$	(B)
$R_y-(CFCl)_n-F$	(C)
$R_xO-(CFCl)_{n-2}-CF=CFCl$	(Q)
$R_xO-(CFCl)_n-Cl$	(E)
$F-[(CFCl)_{n-1}CF_2]-OR_x$	(I)
$R_xO-[(CFCl)_{n-m}(CF_2)_m]-OR_x$	(L)
$R_xO-[(CFCl)_{n-m}(CF_2)_m]-Cl$	(M)
$R_y-[(CFCl)_{n-m}(CF_2)_m]-Cl$	(N)

and mixtures thereof, wherein
R_x is a linear or branched perhaloalkyl, perhaloalkylmonoether or perhaloalkylpolyether radical of from 1 to 10 carbon atoms, which contains fluorine atoms or fluorine and chlorine atoms;
R_y is a linear or branched perhaloalkyl, perhaloalkylmonoether or perhaloalkylpolyether radical of from 1 to 9 carbon atoms, which contains fluorine atoms or fluorine and chlorine atoms;
n ranges from 4 to 20, preferably from 4 to 10; and m is 1 or 2.

12. Mixtures of telomers of 1,2-dichloro-1,2-difluoroethylene, prevailingly containing species of the formulae

$R_xO-(CFCl)_n-F$	(A)
$R_xO-(CFCl)_n-OR_x$	(B)
$R_y-(CFCl)_n-F$	(C)
$F-(CFCl)_n-F$	(D)

wherein R_x, R_y and n are defined as in claim 11.

13. Mixtures of telomers of 1,2-dichloro-1,2-difluoroethylene containing, in addition to the species of formulae (A), (B), (C) and (D), some or all of the species of the following formulae:

$F-(CFCl)_n-F$	(D)
$R_xO-(CFCl)_n-Cl$	(E)
$F-(CFCl)_n-Cl$	(F)
$Cl-(CFCl)_n-Cl$	(G)
$F-[(CFCl)_{n-1}CF_2]-F$	(H)
$F-[(CFCl)_{n-1}CF_2]-OR_x$	(I)
$R_xO-[(CFCl)_{n-m}(CF_2)_m]-OR_x$	(L)
$R_xO-[(CFCl)_{n-m}(CF_2)_m]-Cl$	(M)
$R_y-[(CFCl)_{n-m}(CF_2)_m]-Cl$	(N)
$F-[(CFCl)_{n-m}(CF_2)_m]-Cl$	(O)
$Cl-[(CFCl)_{n-m}(CF_2)_m]-Cl$	(P)

wherein R_x, R_y, m and n have the meanings given in claim 11.

14. Telomers or mixtures of telomers of 1,2-dichloro-1,2-difluoroethylene according to any one of claims 11 to 13, characterized in that, when R_x and R_y are perhaloalkylpolyether radicals, they contain two oxygen atoms.

15. Telomers or mixtures of telomers of 1,2-dichloro-1,2-difluoroethylene according to any one of claims 11 to 14, characterized in that R_x and R_y are perfluorinated radicals or that, when R_x and R_y contain chlorine atoms, said radicals do not comprise $-CCl_3$ groups.

16. Telomers or mixtures of telomers of 1,2-dichloro-1,2-difluoroethylene according to any one of claims 11 to 15, characterized in that R_x contains from 1 to 6 and R_y contains from 1 to 5 carbon atoms.

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(54) Telomers of 1,2-dichloro-1,2-difluoroethylene and process for preparing them.

(57) The present invention relates to telomers of 1,2-dichloro-1,2-difluoroethylene and to a process of preparing them.

1,2-dichloro-1,2-difluoroethylene is reacted, at a temperature of from -100° C to +50° C, with a perhalofluorooxy compound of formula

R_x-OF

wherein

R_x represents, among other, a perhaloalkyl radical of from 1 to 10 carbon atoms.

Telomers are obtained which have, among others, the formulae

R_XO-$(CFCl)_n$-F

R_xO-$(CFCl)_n$-OR_x

R_y-$(CFCl)_n$-F and

F-$(CFCl)_n$-F,

wherein

R_y represents, among others, a perhaloalkyl radical containing from 1 to 9 carbon atoms.

Most of the resulting telomers are new products.

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European Patent Office

EUROPEAN SEARCH REPORT

Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 321 990 (AUSIMONT) * Claims *	1-16	C 07 C 43/12 C 07 C 43/17 C 07 C 19/08
A	GB-A-2 148 286 (OCCIDENTAL) * Claims *	1-16	C 07 C 41/06 C 07 C 17/26
A	EP-A-0 267 626 (AUSIMONT) * Column 2, lines 29-39; claims *	1-16	
A	EP-A-0 267 627 (AUSIMONT) * Claims *	1-16	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 07 C 17/00
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C 07 C 41/00
C 07 C 43/00

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	15 March 91	ZERVAS B.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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A: technological background
O: non-written disclosure
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E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

EP 343,038

DIALOG(R)File 351:DERWENT WPI

Cleaning surface of objects using cold plasma - particularly for stainless steel, glass, porcelain or ceramics polluted with oil and grease containing. nuclear elements

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Number of Countries: 018 Number of Patents: 008
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NO--173921 B NO-8901827

Abstract (Basic): EP 343038 A

A process for cleaning the surface of an object made of stainless steel, glass, porcelain or ceramic, pure or mixed, comprises subjecting the object to the action of a deferred cold plasma, for a time sufficient to decompose the polluting materials deposited on the surface of the object.

The plasmagenic gas is a mixt. of dioxygen and dinitrogen, pref. also contg. at most 10% of a fluorinated or chlorinated cpd. (I), esp. NF3, CF4, SF6, F2, NCl3, tetra-, tri- or di-chloromethane or Cl2. The plasmagenic gas is at a pressure of 12 mbar and is a mixt. of 75% dioxygen, 23.5% dinitrogen and 1.5% of the cpd. (I).

USE - For removing polluting materials such as mechanical oils or greases form e.g. tools used in the nuclear industry. The plasma does not adversely effect the object being cleaned.

Title Terms: CLEAN; SURFACE; OBJECT; COLD; PLASMA; STAINLESS; STEEL; GLASS;
PORCELAIN; CERAMIC; POLLUTION; OIL; GREASE; CONTAIN; NUCLEAR; ELEMENT
Derwent Class: K08; L01; L02; M13; P43
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